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Date: 15 May 1968

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Washington, D. C. 20550

Reports Required

Annual - Short informal
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Final - Comprehensive report
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Assigned to: School of Chemistry

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RESEARCH PROJECT TERMINATION

Date: November 25, 1970

Project Title: Polynuclear Complexes of Metal Alkoxides

Project No.: B-1531

Principal Investigator: Dr. J. A. Bertrand

Sponsor: National Science Foundation

Effective Termination Date: December 1, 1970

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Georgia Institute of Technology
Atlanta, Georgia 30332
August 23, 1969



FIRST ANNUAL TECHNICAL REPORT

NSF GP-8475

POLYNUCLEAR COMPLEXES OF METAL ALKOXIDES

Submitted by

J. Aaron Bertrand, Jr.
Associate Professor
School of Chemistry

INTRODUCTION

During the first year of this grant, several types of polynuclear complexes have been investigated; these have included dimers, trimers, and tetramers with μ_4 -, μ_3 -, and μ_2 -bridges. Although the title of the grant does not include the possibility of μ_4 -bridges, several μ_4 -oxo complexes have been studied since their properties are important to an understanding of the properties of bridging oxygens.

Most of the work during the first year has been in the areas of magnetic interactions and unusual coordination symmetries. In the area of magnetic interactions, the determination of structures for several copper complexes has provided a correlation between structure and magnetic properties; in the area of unusual coordination symmetries, a structure determination has provided the first example of a trigonal-prismatic complex with oxygen donors and has suggested the possibility of similar complexes with different metal ions.

EXPERIMENTAL RESULTS

μ_4 -Oxo Complexes.- Previous work in these laboratories had produced several complexes of the general formula $\text{Cu}_4\text{OX}_6\text{L}_4$ where X = halide and L = monodentate ligand; complexes with X = Cl, Br and L = triphenylphosphine oxide, pyridine N-oxide had been prepared and the structure of the compound with X = Cl and L = triphenylphosphine oxide had been determined here^{1,2}; the structure of the compound with X = Cl and L = pyridine was determined by other workers³. The two structures are very similar; as in CuO , the oxygen is tetrahedrally surrounded by four coppers and the Cu - Cu

distances in these two complexes and in CuO are identical. To determine how constant the Cu - Cu distance would be in related compounds, the structures of the compound with X = Cl and L = Cl⁴ and the compound with X = Br and L = NH₃ were determined. In both of these structures, the Cu - Cu and Cu - O distances were identical to those of the previous structures. In the bromide structure, the only effect of the greater Cu - Br distance was to decrease the bond angle at bromine.

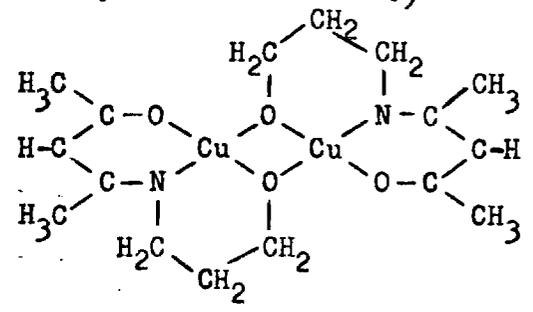
Although we had previously prepared other bromide complexes, no structures had been done due to problems in obtaining single crystals. The preparation of Cu₄OBr₆(NH₃)₄ was accidental; the compound resulted from attempts to recrystallize polynuclear aminoalkoxide complexes, CuBr(OCH₂CH₂NR₂). The compound has also been prepared from CuCl₂(RNH₂)₂ compounds; studies are in progress to identify the organic by-products of this reaction.

μ_3 -Bridged Cubane-type Complexes.- A series of compounds of the general formula [M(Acac)(CH₃O)(CH₃OH)]₄, where M = Co, Ni, or Mg, and Acac represents the anion of 2,4-pentanedione, were found to have a cubane-type structure. A second crystalline form of the cobalt compound was isolated and it was thought to contain an isomer with a different arrangement of the chelate groups. A structure determination has revealed that this tetragonal form contains molecules identical to those found in the monoclinic crystals; the higher symmetry results from a different packing arrangement in which the individual molecules are disordered.

A nickel complex in which the 2,4-pentanedione anion is replaced by the anion of salicylaldehyde has been studied by other workers⁵ and found to

Coordination about nickel is square-planar; the four-membered ring is considerably bent, presumably because of steric limitations of the ligand. A planar four-membered ring was achieved in the corresponding copper complex by forcing the nitrogen atom out of the plane of the copper and coordinated oxygens; the ligand field stabilization of square-planar nickel, which results in a spin-paired arrangement, apparently maintains the planar coordination and forces the bending of the four-membered ring.

Since the steric limitations of the ligand seemed to affect the structures of these complexes, complexes were prepared with the corresponding propanol-imine, abbreviated PIA in formulas. The copper complex, Cu(PIA), was found, by a single crystal x-ray diffraction study,⁹ to be a dimer:



Coordination about copper is square-planar, the four-membered ring is planar, and the carbon bonded to the bridging oxygen is in the same plane as the four-membered ring.

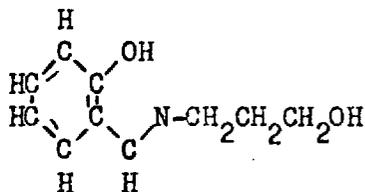
It is interesting that a low magnetic moment, 0.41 B.M., was observed for $[Cu(PIA)]_2$ while normal moments were observed for $[Cu(EIA)]_4$ and the μ_4 -oxo complexes. Comparison of the structures shows two important differences: (1) in $[Cu(PIA)]_2$ copper is four-coordinate while in $[Cu(EIA)]_4$ and the μ_4 -oxo complexes copper is five-coordinate; (2) in $[Cu(PIA)]_2$ the bridging oxygen atoms use three outer orbitals for sigma-bonding and exhibit planar coordination about the oxygens while in $[Cu(EIA)]_4$ and the μ_4 -oxo complexes the

bridging oxygen atoms use all four outer orbitals for sigma-bonding and exhibit tetrahedral coordination.

Compounds of the general formula $\text{CuX}(\text{OCH}_2\text{CH}_2\text{NR}_2)$ have been reported; some of the compounds reported have normal moments and others have low moments. It appears likely that the same structural differences occur in these compounds and structure studies of two of these are in progress.

The planar three-coordinate arrangement about the bridging oxygens in $[\text{Cu}(\text{PIA})]_2$ suggests pi-symmetry for the fourth outer orbital and supports the suggestion that the electrons are coupled through a pi-mechanism. The overlap of the oxygen pi-orbitals and the d_{xz}, d_{yz} orbitals of the coppers would produce pi-molecular orbitals delocalized over the four-membered ring; in the ground state, one anti-bonding molecular orbital would be vacant but at room temperature thermal population of this orbital would occur and paramagnetism would be observed.

However, there is still the possibility that the coordination about copper is the factor which accounts for the difference in magnetic properties of these compounds and attempts have been made to prepare a low-moment compound with five-coordinate copper. Copper complexes of II with one and two



protons removed have been prepared and both have low magnetic moments. The complex with one proton removed has a chloride ion to balance the charge of

the copper ion and the copper is presumed to be five-coordinate. Structure studies of both of these complexes are in progress and these should provide further information about the mechanism of coupling.

As another means of testing the pi-bonding hypothesis, the preparation of complexes of II with other metal ions has been attempted; the complex of iron(III) has been prepared and the low magnetic moment observed, 3.9 B.M., indicates coupling of electrons between metal ions in this complex. A structure study on this compound is in progress.

μ_2 -Bridged Trimers.- Several complexes of cobalt and 2-aminoethanol have been reported but no magnetic or structure studies had been done. We prepared the acetate salt of $\text{Co}_3(\text{ETA})_6^{2+}$ (ETA represents the anion of 2-aminoethanol), determined its magnetic moment, and carried out a structure determination¹⁰. The complex consists of two tris-chelates of cobalt(III) sharing faces with a cobalt(II) ion; the coordination of the cobalt(III) ions is octahedral but the cobalt(II) has trigonal-prismatic coordination. This is the first example of a spin-free trigonal-prismatic complex. The complex corresponds to an optically active isomer and attempts are being made to isolate the optically inactive isomer for a structure study; molecular models suggest that the optically active isomer is forced into trigonal-prismatic coordination by steric factors and the inactive isomer may be octahedral.

We have oxidized the central cobalt(II) to cobalt(III) and isolated salts of $\text{Co}_3(\text{ETA})_6^{3+}$. We have also replaced the central cobalt(II) with nickel(II) and we are currently attempting to prepare complexes with other metal ions.

A structure study of the cobalt(III) complex is necessary to establish the coordination symmetry in that complex; so far, suitable single crystals have not been obtained.

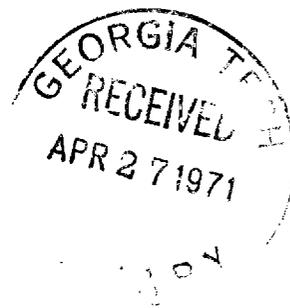
Spectral studies of these complexes are in progress; these should be very interesting since it is possible to compare ligand field predictions with observed spectra for this unusual type of coordination.

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B-1531

Georgia Institute of Technology
Atlanta, Georgia 30332
July, 1970



FINAL TECHNICAL REPORT

NSF GP-8475

June 1, 1968-May 31, 1970

POLYNUCLEAR COMPLEXES OF METAL ALKOXIDES

Submitted by

J. A. Bertrand

Associate Professor of Chemistry

Introduction

A number of oxygen-bridged complexes of the first transition series metal ions are known; these complexes have interesting structures and unusual spectral, magnetic, and chemical properties. The relationship between the structures and properties of such complexes is of considerable interest and an understanding of this relationship has been the objective of this study.

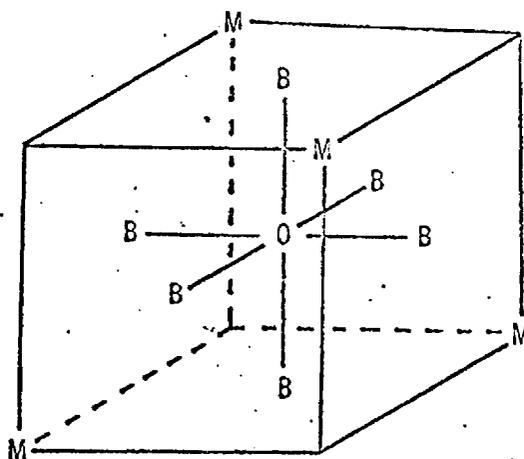
There are a variety of structures possible for such complexes depending on the stereochemistry of the bridging oxygens, the number of bridges between adjacent metal ions, the coordination number and coordination symmetry of the metal ion, and the number of metal ions within the polynuclear unit. As part of this study, a literature survey was made to identify the types of oxygen-bridged complexes that have been observed and to find references to compounds which may contain oxygen bridges but for which structures are not known.

The magnetic properties of polynuclear complexes are of particular interest since within such complexes there are several possible types of magnetic interactions. In order to study the relationship between structure and magnetic properties, we have worked closely with several groups that have facilities to study magnetic properties at low temperatures; joint studies with two of these groups have been accepted for publication and samples of other new compounds have been sent to these groups and to other groups for study.

Stereochemistry of the Bridging Oxygen

Depending on the number of groups and the hybridization of the oxygen orbitals, the arrangement of the groups bonded to oxygen may be tetrahedral (sp^3 hybridized), pyramidal (sp^3 hybridized with a lone pair of electrons), planar-triangular (sp^2 hybridized), bent (sp^3 or sp^2 hybridized), or linear (sp hybridized); examples of all of these have been observed with metal ions of the first transition series.

Tetrahedral coordination by four metal ions is found in the μ_4 -oxo complexes, I, in which a tetrahedron of metal ions, M, surrounds an oxide ion; additional bridging groups, B, bridge pairs of metal ions and are located above the six edges of the tetrahedron. Complexes with carboxylate ions as bridging groups have been prepared for beryllium(II)¹, zinc(II)², and cobalt(II)³; in these complexes, the metal ions are tetrahedrally coordinated. The pivalate complex of cobalt(II)³ has a magnetic moment (3.86 B.M.) considerably below the usual tetrahedral value (4.4-4.8 B.M.) for cobalt(II)



I

complexes but equal to the spin-only value for three unpaired electrons. As part of this study, the copper(II) compound with acetate bridges, $Cu_4O(Ac)_6$,

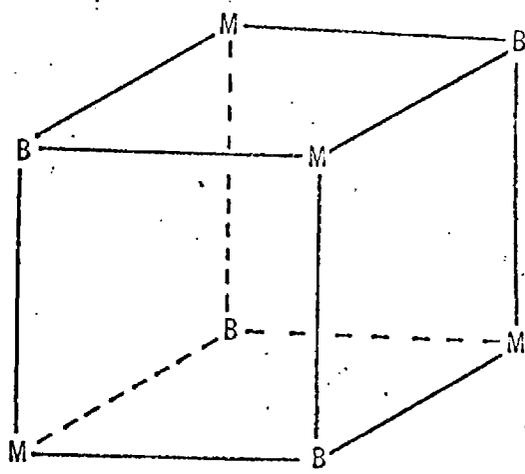
was prepared⁴; magnetic studies have not been made on this compound at the present time.

A series of complexes of the general formula $M_4OB_6L_4$ has been reported for copper(II); the bridging groups are halide ions and the L groups, representing triphenylphosphine oxide⁵, pyridine⁶, pyridine oxide⁴, ammonia⁷, chloride⁸, or 2-methylpyridine⁹, complete the trigonal-bipyramidal coordination of each copper. The room temperature magnetic moments of these complexes are normal but a low temperature study¹⁰ of the chloride-bridged triphenylphosphine oxide complex indicated ferromagnetic (down to 55°K.) and antiferromagnetic (below 55°K.) interactions; since the metal-metal distance is over 3 Å., indirect interactions seem probable. Low temperature studies of the other complexes are in progress¹¹.

It is interesting that the Cu-O distance (1.90) is the same for all of these compounds. Since the Cu-Cl (2.40) distance is greater than the Cu-O distance, the bond angle at the bridging chloride (81°) is less than that at oxygen (109°); in the case of the bromide bridges⁷, this effect is even more apparent with the bond angle at the bridging bromide closed to 76°.

A similar complex with magnesium¹², $Mg_4OBr_6(Et_2O)_4$, and one with cadmium⁴, Cd_4OCl_{10} , have been prepared but attempts to prepare similar complexes with transition metal ions other than copper have not been successful.

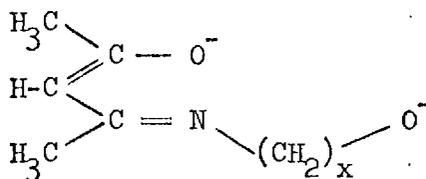
A tetrahedral arrangement of bonded groups around oxygen also occurs in the "cubane-type" complex, II, in which each alkoxide oxygen is bonded to a carbon atom and coordinated to three metal ions; the structure can be described as a tetrahedron of metal ions, M, with bridging groups, B, above each face of the tetrahedron. In addition to oxygen as the bridging group, this type of complex has been observed for iodine-bridged complexes¹³ ($Cu_4I_4L_4$ where L



II

represents tertiary phosphines and arsines) and has been assumed¹⁴ for sulfur-bridged complexes such as $Zn_4(Et)_4(t-Bu-S)_4$.

Methoxide complexes of the general formula $M_4(AA)_4(CH_3O)_4(ROH)_4$ (where M represents cobalt(II), nickel(II), or magnesium(II); AA represents the anion of acetylaceton^{15,16}, salicylaldehyde^{15,17,18}, or o-hydroxyacetophenone¹⁵; and R represents an alkyl group) have a "cubane" structure in which the metal ion is octahedrally coordinated by three bridging oxygens, two oxygens from the bidentate ligand, AA, and an alcohol oxygen. Removal of the alcohol from these complexes yields a tetramer which is presumed to have a "cubane" structure with five-coordinate metal ions; a five-coordinate structure of this type has been observed¹⁹ for $M_4(EIA)_4$ where M represents copper(II) or cobalt(II) and EIA represents the dianion, IIIa, of acetylaceton and 2-amino-1-ethanol; in these complexes, the metal coordination, although somewhat distorted, is best described as trigonal-bipyramidal.

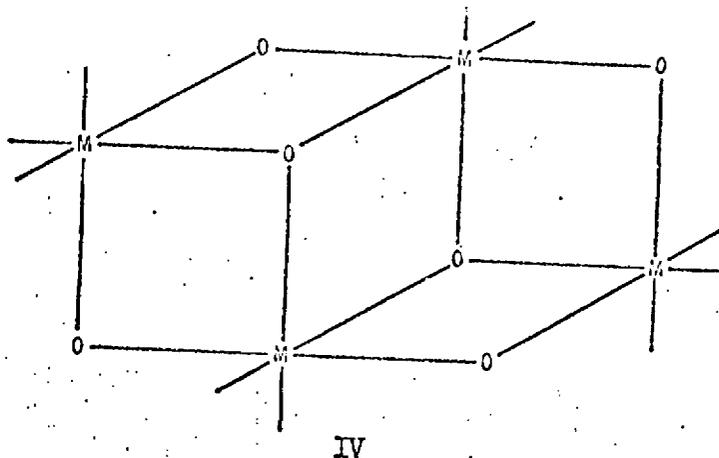


IIIa, $x = 2$; IIIb, $x = 3$

The room temperature magnetic moments of all of the "cubane" complexes are normal but low temperature studies have indicated ferromagnetic interactions in the nickel complexes^{16,18}, and antiferromagnetic interactions in $\text{Cu}_4(\text{EIA})_4$ ¹¹; studies of the cobalt complexes are in progress¹¹.

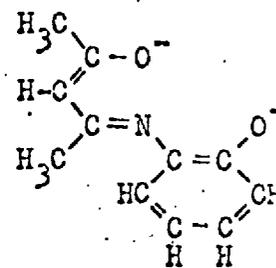
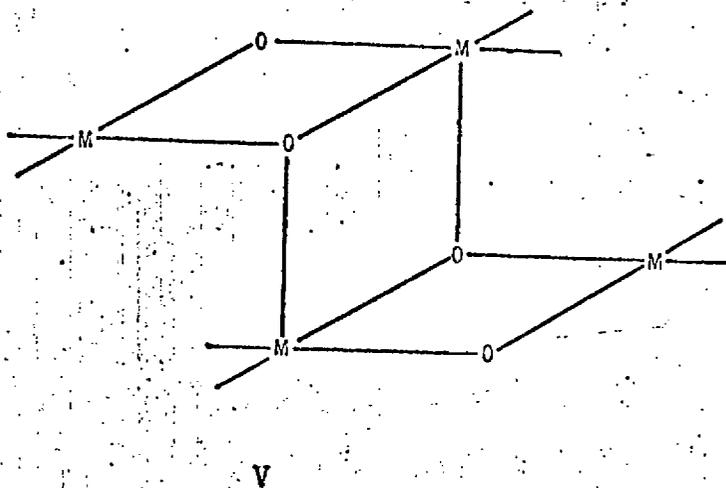
The cobalt(II) and nickel(II) methoxide complexes with various primary alcohols coordinated were prepared^{4,18} by refluxing the methoxide-methanol complexes in other alcohols; although the methanols were readily exchanged, the methoxides did not show exchange even after prolonged heating. Treatment of the dimeric copper(II) methoxide complex, $[\text{Cu}(\text{Acac})(\text{OCH}_3)]_2$, with primary alcohols lead to rapid exchange of the methoxides while treatment with secondary or tertiary alcohols gave crystals of $\text{Cu}(\text{Acac})_2$ —presumably from disproportionation⁴; these results seemed to indicate a relationship between the type of bridging and the lability of the bridging group. However, recent studies⁴ of the reactions of the magnesium complex, which is isostructural with the cobalt and nickel cubanes, indicate that disproportionation occurs readily and factors other than the type of bridging are apparently involved.

Although "cubane" complexes can be prepared, this type of structure is rather strained; the M-O-M bond angles approach 90° rather than the expected tetrahedral value of 109° . This strain can be partially relieved by forming a "displaced dimer" structure, IV, if other groups capable of bridging are present.



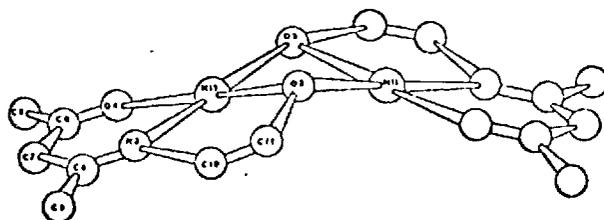
This type of structure has been observed for several titanium(IV) alkoxides²⁰; the structure contains two μ_3 -oxygens and four μ_2 -oxygens. The remaining alkoxide groups are terminal and complete the octahedral coordination of the titanium(IV) ions.

A similar structure has been observed for some copper(II) complexes. In the o-hydroxyanil copper(II) complex²¹, V, there are two μ_3 -oxygens and two μ_2 -oxygens; this structure differs from the previous structure in the number of μ_2 -bridges —the oxygen of the acetylacetonate portion of the ligand, VI, is



not coordinated. The magnetic moment of the copper(II) ions of the tetramer, 1.37 B.M., indicates considerable interaction and a study²² of the temperature dependence of the magnetic susceptibility indicates that the greatest exchange occurs between copper ions bridged by the μ_2 -oxygen. The same type of structure²³ has been found for the compound $\text{Cu}_4(\text{Acac})_4(\text{OCH}_2\text{-C}_6\text{H}_5)_4$. A similar structure was found²⁴ for $[\text{Cu}_4(\text{OH})_4(\text{CH}_3\text{NH}_2)_8(\text{H}_2\text{O})_2]$; the coordination of the waters makes all copper(II) ions five-coordinate. The four-membered ring is not planar in the latter compound and the Cu-Cu distance is 2.78 Å. Magnetic studies have not been reported for this compound.

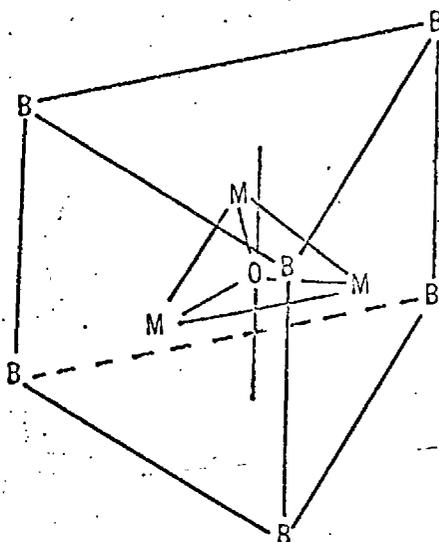
A pyramidal arrangement of the groups bonded to oxygen is observed²⁵ in dimeric $\text{Ni}(\text{EIA})$, VIII. In this structure, the oxygen is bonded to a carbon



VIII

and to two nickel(II) ions in a pyramidal arrangement; if the lone pair of electrons is considered as a fourth group, the arrangement is tetrahedral. Each nickel shows square-planar coordination and the complex is diamagnetic; the four-membered nickel-oxygen ring is considerably bent and the short metal-metal distance, 2.69 Å., suggests the possibility of a metal-metal interaction.

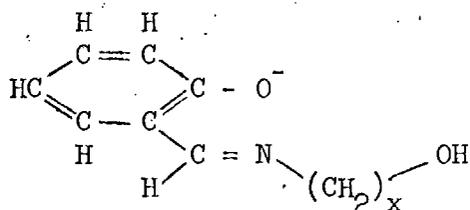
A planar-triangular arrangement of groups about oxygen is found in the μ_3 -oxo complexes, IX. Complexes with the formula $\text{M}_3\text{O}(\text{Ac})_6^+$ have been isolated for iron(III) and chromium(III) and consist^{26,27} of an oxide ion at the center



IX

of an equilateral triangle of metal ions with two acetates bridging each edge of the triangle. Magnetic studies²⁸ of these complexes show an anti-ferromagnetic interaction at room temperature and at lower temperatures; the planar coordination of oxygen indicates that one p-orbital of oxygen is not involved in σ -bonding and a four-centered π -interaction between the metal ions and the central oxygen is possible.

Several dimeric copper(II) complexes show planar coordination about oxygen. In all of these, there is a planar four-membered copper-oxygen ring; all of these show low moments in agreement with the suggestion that a π -interaction leads to more effective coupling of electrons between the two metal ions. In $\text{Cu}_2\text{Cl}_4(\text{PyO})_2$ ²⁹ the copper is tetrahedrally coordinated, the bridging group is a pyridine oxide oxygen, and the magnetic moment is 0.85 B.M.; in $\text{Cu}_2(\text{PIA})_2$ ¹⁹ (where PIA represents the dianion IIIb), the copper is square-planar coordinated, the bridging group is an alkoxide oxygen, and the magnetic moment is 0.41 B.M.; in $\text{Cu}_2(\text{SalPAH})_2\text{Cl}_2$ ³⁰ (where SalPAH represents the anion Xa) the copper is trigonal-bipyramidal coordinated, the bridging group is a phenol oxygen, and



the magnetic moment is 1.1 B.M. These results could indicate a relationship between the lowering of the magnetic moment and the coordination of copper or a relationship between the lowering of the magnetic moment and the electron density at oxygen; results³¹ for a series of complexes with substituted pyridine oxides support a relationship between magnetic moment and electron density at the oxygen.

A dimeric iron(III) complex with planar coordination about oxygen has been prepared and studied.³² The formula is similar to that of the copper(II) chloride complex of the imine of salicylaldehyde and 3-aminopropanol; to balance the higher charge of the iron(III), the alcohol proton is removed. The dimer occupies a site of inversion symmetry and the four-membered ring is, thus, planar; the alcohol oxygen is the bridging group in this compound and its coordination is essentially planar. Magnetic studies at low temperatures indicate a singlet ground state for the dimer. Comparison of the magnetic properties to the properties of an oxygen-bridged iron(III) compound $[\text{Fe}(\text{Sal-en})\text{Cl}]_2$, in which the oxygen coordination is non-planar³³ again suggests the importance of a π -interaction mechanism for spin-coupling.

A linear arrangement of the groups bonded to oxygen provides the possibility of two orthogonal three-centered π -interactions; the diamagnetism of $\text{Ru}_2\text{OCl}_{10}^{4-}$ has been interpreted³⁴ in terms of π -bonding and similar arguments

have been used to explain the bonding in several molybdenum complexes³⁵. In the first transition series metal ions, this arrangement has been observed³⁶ for some iron(III) complexes which show anomalous magnetic properties³⁷. The same arguments have been used to explain⁵ the linear Cu-O-P arrangement in $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$.

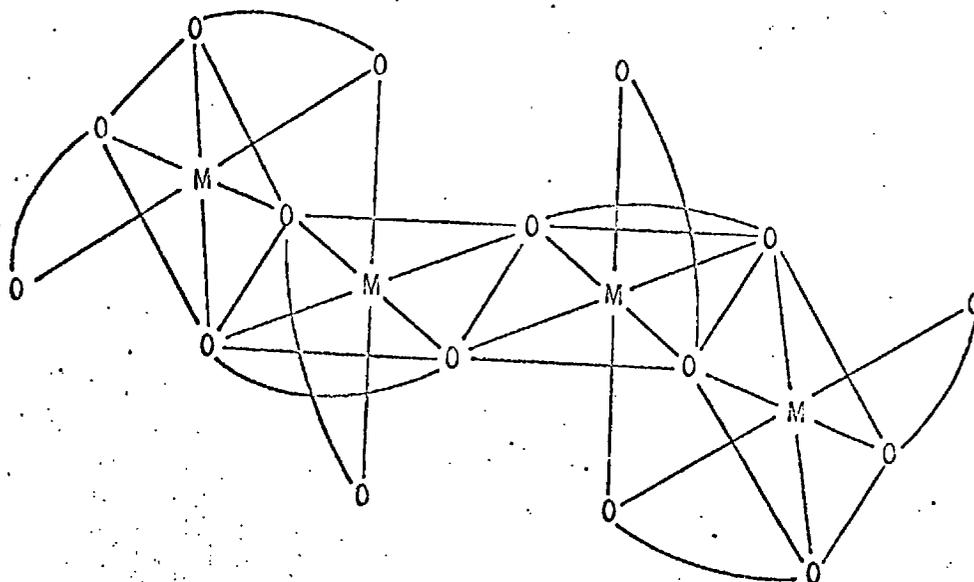
Since structure data were not available for other triphenylphosphine oxide complexes, it was not possible to compare the effect of steric factors and electronic factors on the Cu-O-P arrangement in $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$. The difference in P-O stretching frequencies of $\text{Cu}_4\text{OCl}_6(\text{TPPO})_4$ and $\text{CuCl}_2(\text{TPPO})_2$ was discussed in terms of a linear and bent Cu-O-P arrangement and a difference in π -bonding; a bent arrangement was assumed for the latter compound. The structure of $\text{CuCl}_2(\text{TPPO})_2$ has now been determined⁴; the complex occupies a site of 2-fold symmetry and is tetrahedral as expected. The Cu-O-P arrangement is bent as was assumed, the angle at oxygen is 151° .

Types of Sharing Between Metal Ions

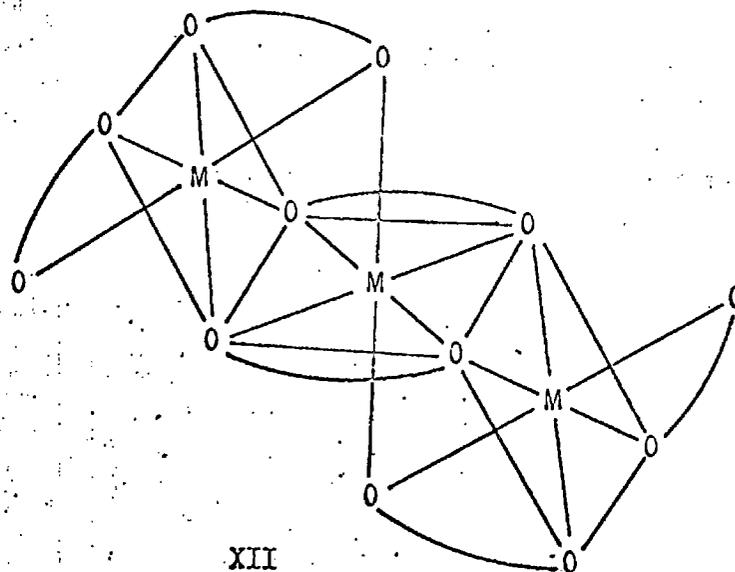
Pairs of metal ions may be bridged by one, two, or three groups corresponding to sharing a corner, an edge, or a face of their coordination polyhedra. In cases where a corner or an edge is shared, multi-centered π -interactions are possible; in cases where an edge or a face is shared, the metal ions may approach close enough for a direct metal-metal interaction. Other factors, such as steric requirements of the ligand and electronic configuration of the metal ions, are important in considerations of the type of sharing; chelate complexes which show molecular association are good examples for investigating such factors:

Both face-sharing and edge-sharing are observed³⁸ in tetrameric cobalt(II) acetylacetonate, XI, in which the terminal cobalt ions share faces with the

inner cobalt ions and the two inner cobalt ions share an edge. In trimeric nickel(II) acetylacetonate, XII, only face-sharing occurs³⁹. In both structures,



XI



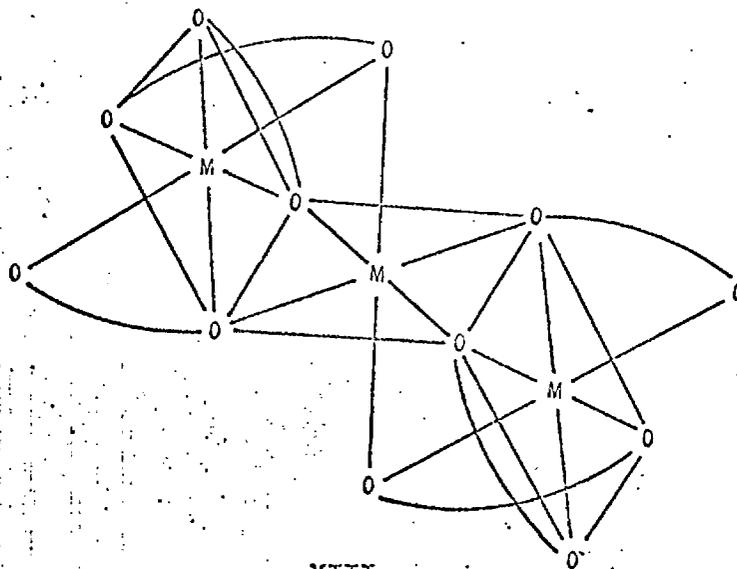
XII

all metal ions are octahedrally coordinated and there are two chelate ligands attached to each metal ion. In trimeric zinc(II) acetylacetonate⁴⁰ only edge-sharing occurs but two of the metal ions are five-coordinate; again, there are two chelate ligands attached to each metal ion.

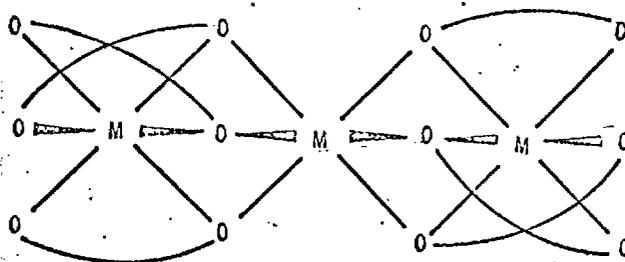
Although magnesium acetylacetonate has been reported, there is little information in the literature on this compound; because of the similarity of the structures of the cobalt, nickel, and magnesium methoxide complexes, $[M(\text{Acac})(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$, further studies of $\text{Mg}(\text{Acac})_2$ were initiated. Although not previously reported, the compound as usually prepared crystallizes as the dihydrate⁴; the dihydrate is isostructural with the corresponding cobalt and nickel compounds and is, thus, the trans-isomer. Crystals of the anhydrous compound have been prepared by sublimation and the structure is being investigated.

Various adducts of metal acetylacetonates have been investigated; a dimeric complex of cobalt(II) acetylacetonate and cyclohexylamine (Cha in formulas) was reported earlier⁴¹. The structure of $[\text{Co}(\text{Acac})_2(\text{Cha})]_2$ has now been completed⁴; as in the corresponding hydrate⁴², the octahedrally coordinated cobalt ions share an edge. The arrangement of the ligands corresponds to that of the center two cobalts of the tetrameric structure XI with cyclohexylamine nitrogens replacing the oxygens donated by the terminal cobalts.

Face-sharing also occurs⁴³ in $\text{Co}_3(\text{DEFAM})_6$ (where DEFAM represents the anion of diethoxyphosphonylacetylmethane), XIII, but the terminal metal ions are chelated by three ligands and the central metal ion is not chelated by any of the ligands — the complex may be thought of as two tris-chelates acting as tridentate ligands toward the central metal ion; each metal ion is octahedrally coordinated. The difference between this complex and the metal acetylacetonates appears to be related to the unsymmetrical ligand which has a lower bridging tendency for the P-O group than for the C-O group; this difference in bridging tendency could be either electronic or steric.



XIII



XIV

A similar structure was found⁴⁴ for $\text{Co}_3(\text{ETA})_6^{2+}$ (where ETA represents the anion of 2-amino-1-ethanol), XIV, in which two tris(2-amino-1-ethoxido)cobalt(III) complexes act as tridentate ligands toward the central cobalt(II); the coordination about the central cobalt(II) is trigonal-prismatic rather than octahedral, presumably due to steric effects. With amino-alkoxide ligands, only one end of the ligand is capable of bridging. The same complex is formed from cobalt(II) or cobalt(III) as starting material; complexes with different metal ions as the central metal ion have been prepared⁴. In the complex, there is an unusually short metal-metal distance, 2.60 Å., and there is a possibility of direct interactions.

A compound with the formula $\text{NiCo}(\text{ETA})_6\text{I}_2$ has been prepared and studied⁴; the magnetic moment corresponds to two unpaired electrons and suggests a nickel(II) and a cobalt(III) ion. The structure determination⁴ revealed tris-chelates of nickel and cobalt held together by hydrogen bonding; the oxygen faces of the two tris-chelates are arranged to form an octahedron of oxygen atoms. To balance charges, three protons must be present and the short oxygen-oxygen distances between the tris-chelates indicates strong hydrogen bonding. Neutron diffraction studies to determine the hydrogen positions are planned.

A number of cobalt(III)⁴⁵⁻⁴⁷ and chromium(III)⁴⁸ compounds of the general formula $\text{M}_2(\text{ETA})_6\text{X}_3$ have been reported and at least one investigator⁴⁶ suggested hydrogen-bonded dinuclear units. It is probable that these compounds have the same hydrogen-bonded structure found for the nickel-cobalt compound.

The Relationship Between Structure and Magnetic Properties

In some polynuclear complexes, the arrangement and type of bridging make it possible for two or more metal ions to approach each other closely enough for direct overlap of metal orbitals; in the case of metal ions with unpaired electrons in these orbitals, total or partial pairing of electron spins would occur between metal ions. In polynuclear complexes which show metal-metal separations large enough to make the importance of direct overlap questionable, there is still the possibility of multi-centered overlap between orbitals on the metal ions and orbitals on the bridging groups; such overlaps could also lead to total or partial pairing of electrons between metal ions.

Although both σ - and π -type delocalized interactions are possible, a survey of the available data on oxygen-bridged complexes strongly suggests that π -type interactions are much more effective in pairing electrons; in all cases where a reduced magnetic moment has been observed at room temperature

for an oxygen-bridged complex, structure studies have revealed either a short metal-metal distance or an arrangement of groups about the bridging oxygen which dictates that one or two p-orbitals of oxygen are not involved in σ -bonding and are thus available exclusively for π -bonding to the metal ions. In cases where all outer orbitals of oxygen are involved in σ -bonding, magnetic interactions have been observed only at lower temperatures; thus, a less effective mechanism of spin-pairing is indicated for such cases.

In some cases, spin-coupling has been discussed in terms of π -bonding—the diamagnetism of $\text{Ru}_2\text{OCl}_{10}^{4-}$ has been explained in terms of two three-centered π -interactions and the spin-coupling in $\text{M}_3\text{O}(\text{Ac})_6(\text{H}_2\text{O})_3^+$ complexes has been related to the delocalized π -system. In this study, a number of complexes which exhibit sub-normal magnetic moments have been investigated and found to contain a planar four-membered metal oxygen ring.^{19,32} Using the treatment of $p\pi$ - $d\pi$ bonding proposed for other⁴⁹ cyclic systems, it is possible to explain the spin-coupling in these complexes.

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"The Crystal and Molecular Structure of Dichlorobis(triphenylphosphine oxide)-copper(II)," J. A. Bertrand and A. R. Kalyanaraman.

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